

EFFECT OF SODIUM CHLORIDE ON THE APPARENT IONIZATION CONSTANT OF BORIC ACID AND THE pH VALUES OF BORATE SOLUTIONS

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ABSTRACT

The pH values for solutions of borax (sodium tetraborate decahydrate) and sodium chloride were determined from 0° to 60° C by the method of cells without liquid junction. In one series, the effect of sodium chloride on the apparent ionization constant of boric acid was determined by measurements of cells in which the concentration of borax was maintained constant (0.01*m*) while that of the sodium chloride was varied. In a second series, the pH values of various concentrations of borax in 0.01-*m* sodium chloride were measured, and in a third, similar measurements were made of solutions containing 0.025-*m* borax with a variable concentration of chloride.

The values of other investigators for the pH of solutions of borax in which cells with liquid junctions were involved are compared with those currently reported. Some of these are modified to take cognizance of present-day views concerning electrolytic dissociation.

A 0.01-*m* solution of borax (3.81 g of borax per liter of solution) is recommended for the calibration of pH equipment. The equation

$$\text{pH} = 2331.7/T + 0.017433T - 3.840,$$

where *T* is the absolute temperature, represents the pH values for this solution from 0° to 60° C.

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I. INTRODUCTION

In an earlier communication [1]¹, data were presented from 0° to 60° C for the ionization constant of boric acid and the pH values of solutions composed of stoichiometrically equal ratios of boric acid, sodium borate, and sodium chloride. For the reversible functioning of the silver-silver-chloride electrodes used in the determination of pH by the method of cells without liquid junction [2], the presence of an alkali chloride is necessary. However, buffer solutions for in

¹ Figures in brackets indicate the literature references at the end of this paper.

checking or calibrating instruments for the measurement of pH are more conveniently prepared without the alkali chloride. For this reason there was made a study of the effect of sodium chloride on the pH of solutions of borax.

In this paper measurements are reported of the emf from 0° to 60° C, at intervals of 5 degrees, of hydrogen and silver-silver-chloride electrodes immersed in three series of buffer-chloride solutions and the calculations of the pH values of these mixtures.

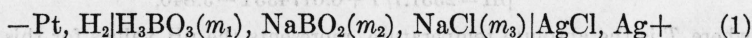
Series *A* contained 0.01 mole of borax (sodium tetraborate) and from 0.008 to 0.08 mole of sodium chloride per kilogram of water.

In series *B* the concentration of chloride ion was kept constant at 0.01 *m*, whereas that of the borax was varied progressively from 0.004 to 0.05 *m*. In series *C* the concentration of borax was kept constant at 0.025 *m*, whereas that of the chloride was varied from 0.005 to 0.05 *m*. Comparisons were made with the data of Owen [3] for concentrated solutions of borax in sodium chloride. At the same concentrations, both sets of data for the values of the negative of the common logarithm of the apparent ionization constant of boric acid agree to within ± 0.002 .

The apparatus and the experimental procedure used have been described previously [1]. Distilled water having a specific conductance at 25° C of 0.5×10^{-6} mho/cm³ was used for the preparation of the solutions.

II. ELECTROMOTIVE FORCE OF GALVANIC CELLS AND THE APPARENT IONIZATION CONSTANT OF BORIC ACID

Measurements were made of the emf of the cell:



at 5-degree intervals from 0° to 60° C.

The electromotive force of the cell in eq 1 is given by

$$E = E^\circ - k \log (a_{\text{H}} f_{\text{Cl}} m_{\text{Cl}}), \quad (2)$$

where E is the measured emf of the cell, E° is the normal potential of the silver-silver-chloride electrode when the activity of the chloride ion is unity [4], k is the value for $(2.3026 RT/F)$ at the temperature of the measurements [5], a_{H} is the activity of the hydrogen ion, and m_{Cl} and f_{Cl} are the molality and the activity coefficient, respectively, of chloride ion. By this method the mean activity coefficient of hydrogen and chloride ions is obtained. To calculate a_{H} , the assumption is made that $f_{\text{H}} = f_{\text{Cl}}$.

The activity of the hydrogen ion is governed principally by the value of the ionization constant, K , of the boric acid,

$$K = (a_{\text{H}} a_{\text{BO}_2}) / (a_{\text{H}_3\text{BO}_3}) \quad (3)$$

and the buffer ratio, $m_{\text{H}_3\text{BO}_3}/m_{\text{BO}_3} = m_1/m_2$, corrected for hydrolysis.

The compositions of the solutions in moles per kilogram of water (vacuum basis) and the emf from 0° to 60° C, corrected to 1 atmosphere of hydrogen are given in table 1.

TABLE 1.—Compositions of the solutions in moles per kilogram of water and the observed emf from 0° to 60° C, in international volts, corrected to 1-atmosphere of hydrogen, for the cells —Pt, H₂|H₃BO₃(m₁), NaBO₂(m₂), NaCl(m₃)|AgCl, Ag+

SERIES A

Cell	m ₁ =m ₂	m ₃	E ₃₀ °	E ₃₅ °	E ₄₀ °	E ₄₅ °	E ₅₀ °	E ₅₅ °	E ₆₀ °	E ₃₀ °	E ₃₅ °	E ₄₀ °	E ₄₅ °	E ₅₀ °	E ₅₅ °	E ₆₀ °
1.....	0.02000	0.007829	0.86644	0.87146	0.87679	0.88229	0.88778	0.89324	0.89877	0.90439	0.90995	0.91545	0.92101	0.92632	0.93191	0.93191
2.....	.01998	.01118	.85781	.86286	.86802	.87342	.87886	.88402	.88947	.89493	.90028	.90565	.91112	.91644	.92182	.92182
3.....	.02000	.01241	.85547	.86021	.86534	.87067	.87600	.88139	.88674	.89215	.89746	.90280	.90821	.91358	.91884	.91884
4.....	.01998	.01296	.85463	.85943	.86457	.86986	.87516	.88038	.88573	.89109	.89643	.90176	.90719	.91250	.91780	.91780
5.....	.01999	.01618	.84938	.85405	.85906	.86429	.86948	.87461	.87984	.88511	.89037	.89565	.90088	.90611	.91125	.91125
6.....	.02001	.01649	.84847	.85328	.85836	.86358	.86882	.87412	.87940	.88469	.88992	.89518	.90046	.90574	.91089	.91089
7.....	.01998	.01839	.84608	.85085	.85585	.86100	.86615	.87121	.87644	.88166	.88686	.89201	.89729	.90243	.90757	.90757
8.....	.01998	.02011	.84386	.84863	.85362	.85874	.86389	.86895	.87419	.87940	.88464	.88975	.89504	.90018	.90533	.90533
9.....	.02001	.02122	.84267	.84735	.85228	.85738	.86249	.86768	.87279	.87802	.88312	.88828	.89346	.89861	.90372	.90372
10.....	.01998	.02983	.83469	.83917	.84394	.84890	.85385	.85870	.86371	.86873	.87372	.87886	.88388	.88892	.89380	.89380
11.....	.02000	.04125	.82684	.83107	.83573	.84057	.84538	.85032	.85514	.86010	.86492	.86975	.87467	.87957	.88432	.88432
12.....	.01998	.04989	.82228	.82659	.83113	.83587	.84061	.84526	.85005	.85484	.85963	.86435	.86914	.87390	.87862	.87862
13.....	.02001	.07998	.81043	.81465	.81905	.82360	.82813	.83274	.83726	.84193	.84648	.85102	.85559	.86013	.86465	.86465

SERIES B

14.....	0.008941	0.010000	0.85987	0.86521	0.87053	0.87600	0.88144	0.88679	0.89212	0.89772	0.90317	0.90863	0.91414	0.91943	0.92465	0.92465
15.....	.010045	.010008	.86041	.86547	.87062	.87618	.88166	.88700	.89258	.89797	.90339	.90880	.91426	.91960	.92499	.92499
16.....	.011915	.009999	.86000	.86535	.87069	.87610	.88160	.88697	.89234	.89797	.90345	.90892	.91442	.91973	.92498	.92498
17.....	.01490	.010003	.86015	.86548	.87072	.87615	.88168	.88703	.89237	.89801	.90353	.90895	.91454	.91985	.92511	.92511
18.....	.01968	.009999	.86070	.86564	.87085	.87637	.88183	.88723	.89278	.89819	.90360	.90906	.91461	.91999	.92540	.92540
19.....	.01985	.010000	.86040	.86566	.87093	.87635	.88181	.88721	.89254	.89817	.90365	.90915	.91471	.92007	.92534	.92534
20.....	.02978	.010000	.86092	.86616	.87139	.87677	.88222	.88753	.89283	.89838	.90384	.90927	.91483	.92017	.92545	.92545
21.....	.03516	.010002	.86153	.86639	.87148	.87694	.88234	.88773	.89331	.89863	.90396	.90944	.91495	.92038	.92577	.92577
22.....	.03969	.010000	.86170	.86689	.87204	.87736	.88276	.88802	.89332	.89887	.90435	.90976	.91533	.92065	.92591	.92591
23.....	.04979	.009997	.86249	.86730	.87233	.87771	.88303	.88836	.89373	.89910	.90442	.90980	.91531	.92068	.92600	.92600
24.....	.07529	.010003	.86429	.86911	.87399	.87924	.88447	.8896890030	.90549	.91088	.91628	.92160	.92681	.92681
25.....	.09500	.010000	.86557	.87037	.87516	.88041	.88556	.89076	.89607	.90126	.90643	.91173	.91705	.92232	.92759	.92759

SERIES C

26.....	0.05000	0.005015	0.87817	0.88372	0.88928	0.89476	0.90036	0.90591	0.91183	0.91761	0.92330	0.92873	0.93457	0.94042	0.94620	0.94620
27.....	.05000	.009944	.86185	.86723	.87247	.87773	.88302	.88823	.89395	.89957	.90530	.91035	.91567	.92118	.92610	.92610
28.....	.05000	.01983	.84586	.85077	.85562	.86062	.86549	.87023	.87580	.88105	.88624	.89095	.89598	.90124	.90659	.90659
29.....	.05000	.02989	.83588	.84072	.84554	.85030	.85508	.85981	.86498	.87022	.87530	.87984	.88479	.88982	.89494	.89494
30.....	.05000	.04032	.82893	.83359	.83816	.84292	.84748	.85217	.85722	.86226	.86724	.87181	.87656	.88151	.88659	.88659
31.....	.05000	.05001	.82374	.82809	.83252	.83713	.84171	.84627	.85127	.85619	.86096	.86527	.87032	.87482	.87953	.87953

Values of the negative of the common logarithm of the apparent ionization constant (pK') of boric acid were calculated for each temperature and concentration by means of the equation

$$pK' = (E - E^\circ)/k + \log m_{Cl} + \log (m_1/m_2). \quad (4)$$

Plots of pK' at 0°, 25°, and 60° C against the ionic strength, μ , are given in figure 1. Curve *A*, series *A*, shows the results obtained when the concentration of borax was kept constant at 0.01 *m*, whereas that of the chloride was varied; curve *B*, series *B*, is plotted from the data in which the concentration of chloride was maintained at a constant value (0.01 *m*), whereas that of the borax was varied; curve *C*, series *C*, denotes the data obtained when the molality of borax was

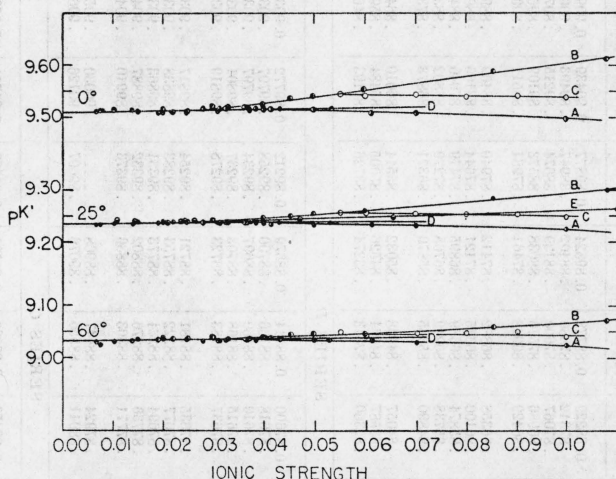


FIGURE 1.—Plots of pK' at 0°, 25°, and 60° C. against the ionic strength.

Curve *A* shows the results obtained when the concentration of borax was kept constant at 0.01 *m*, while that of the chloride was varied (series *A*); curve *B* denotes the points obtained in which the concentration of the borax was varied, while that of the chloride was kept constant at 0.01 *m* (series *B*); curve *C* was computed from the series in which the borax was kept at 0.025 *m*, while the concentration of chloride was varied (series *C*); curve *D* was calculated from the data for stoichiometrically equal ratios of boric acid, sodium borate, and sodium chloride [1]; and curve *E* represents the data of Owen [3] at 25° C for which $m_{\text{Borax}} = 0.5675 \text{ mCl}$.

kept constant at 0.025 and the chloride varied; and curve *D* represents the data obtained for stoichiometrically equal ratios of boric acid, sodium borate, and sodium chloride [1]. For comparison, the data of Owen [3] at 25° C, in which $m_{\text{Borax}} = 0.5675 m_{\text{Cl}}$, are given in curve *E* of figure 1. As expected from the use of this proportion of borate to chloride, curve *E* lies between curves *B* and *D*.

When sodium chloride is added to a solution of borax, the value for pK' is lowered. Within the experimental error of the measurements, the values for pK' for the mixtures of series *A* and *C* can each be represented by straight lines according to an equation of the type

$$pK' = pK'_0 + C m_{Cl}. \quad (5)$$

In eq 5, pK'_0 is the negative of the common logarithm of the apparent ionization constant of boric acid in either a 0.01-*m* or a 0.025-*m*

solution of borax free from sodium chloride, and C is a constant at a given concentration of buffer.

Similarly, the quadratic equation

$$pK' = pK'_0 + D m_{\text{Borax}} + E m_{\text{Borax}}^2 \quad (6)$$

expresses the variation in series B of the negative logarithm of the apparent ionization constant of boric acid in 0.01- m sodium chloride. The values for pK'_0 and for the constants in eq 5 and 6 differ because the extrapolations are made to different ionic strengths, and are given in table 2.

TABLE 2.—Values for the constants from 0° to 60° C in the equations $pK' = pK'_0 + C m_{\text{Cl}}$ (eq 5) and $pK' = pK'_0 + D m_{\text{Borax}} + E m_{\text{Borax}}^2$ (eq 6)

Temp- perature	Equation 5				Equation 6, $m_{\text{Cl}}=0.01$		
	$m_{\text{Borax}}=0.01$		$m_{\text{Borax}}=0.025$		pK'_0	D	E
	pK'_0	C	pK'_0	C			
° C							
0	9.522	-0.23	9.545	-0.22	9.509	1.3	17
5	9.450	-0.22	9.479	-0.21	9.440	1.2	16
10	9.388	-0.21	9.417	-0.20	9.381	1.1	15
15	9.336	-0.20	9.360	-0.19	9.328	1.0	14
20	9.287	-0.19	9.308	-0.18	9.280	0.8	14
25	9.241	-0.18	9.259	-0.17	9.235	.7	14
30	9.201	-0.17	9.222	-0.16	9.196	.7	11
35	9.167	-0.16	9.187	-0.15	9.161	.6	11
40	9.134	-0.16	9.155	-0.14	9.129	.6	9
45	9.108	-0.15	9.122	-0.13	9.102	.6	7
50	9.082	-0.14	9.094	-0.12	9.078	.5	6
55	9.059	-0.13	9.072	-0.11	9.054	.5	5
60	9.038	-0.12	9.049	-0.10	9.033	.5	4

III. pH VALUES OF BORAX-CHLORIDE SOLUTIONS AND THE pH OF SOLUTIONS OF BORAX WITHOUT SODIUM CHLORIDE

The pH values for the solutions of series A and C were calculated from the equation

$$\text{pH} = (E - E^0)/k + \log m_{\text{Cl}} - A\mu^{1/2}/(1 + Ba_i\mu^{1/2}) - C m_{\text{Cl}} \quad (7)$$

where the value for C was obtained from the variation of pK' with ionic strength. A value of 4.4 was used for a_i [1].² The pH of these solutions are expressed more conveniently in terms of the concentration of the added salt by the equation

$$\text{pH}_{(m_{\text{Borax}}=0.01, m_{\text{Cl}}=X)} = \text{pH}_{(m_{\text{Borax}}=0.01, m_{\text{Cl}}=0)} + Fm_{\text{Cl}} \quad (8)$$

in which $\text{pH}_{(m_{\text{Borax}}=0.01, m_{\text{Cl}}=0)}$ denotes the pH of a 0.01- m borax buffer in the absence of sodium chloride. The value of the constant F is obtained by the method of least squares. A similar equation is

² Collateral evidence obtained for phthalate [6], phosphate [7], and phenosulfonate [8] buffers show that apparently a_i is unchanged when the ratio of buffer to sodium or potassium chloride is altered.

obtained for 0.025-*m* borax. Values for the pH of 0.01-*m* and 0.025-*m* solutions of borax calculated from eq 8 and of the corresponding values for *F* are given in table 3.

TABLE 3.—Values for the pH of 0.01-*m* and 0.025-*m* solutions of borax free from sodium chloride and the corresponding values for *F* in eq 8

Temperature	pH (=Borax=0.01- <i>m</i> Cl=0)	<i>F</i>	pH (=Borax=0.025- <i>m</i> Cl=0)	<i>F</i>
°C				
0	9.463	-0.68	9.460	-0.46
5	9.389	-0.66	9.394	-0.46
10	9.328	-0.70	9.331	-0.46
15	9.273	-0.66	9.274	-0.47
20	9.223	-0.66	9.221	-0.47
25	9.177	-0.70	9.172	-0.47
30	9.135	-0.67	9.134	-0.47
35	9.100	-0.70	9.099	-0.47
40	9.066	-0.68	9.066	-0.48
45	9.037	-0.70	9.031	-0.48
50	9.012	-0.72	9.003	-0.48
55	8.987	-0.72	8.980	-0.48
60	8.961	-0.66	8.956	-0.48

Hamer and Acree [9] proposed a method for calculating the pH of buffer-chloride solutions that obviates the necessity of determining either a_i or C . This procedure, once its validity were established, would have much to recommend it, especially in the treatment of univalent buffer mixtures. Hamer and Acree proposed the equation

$$\text{pH} = [-\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}})^{\circ} - P]/Q \quad (9)$$

for the calculation of buffer solutions containing no chloride ion, in which $-\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}})^{\circ}$ represents the limiting value at $m_{\text{Cl}}=0$ of $-\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) = (E - E^{\circ})/k + \log m_{\text{Cl}}$, and P and Q are constants whose numerical values are independent of the pH of the buffer but depend only on the temperature, the nature of the cation, and the ionic strength of the solution. This method was applied by them to the calculation of the pH of 0.05-*m* acid potassium phthalate from 0° to 60° C and compared with the pH calculated by the longer but more rigorous process involving a_i , and C [10]. The difference between the pH values obtained by the longer and the shorter methods varied from +0.005 to -0.004 pH unit from 0° to 60° C.

The pH of 0.01-*m* and 0.025-*m* solutions of borax free from sodium chloride were calculated with the use of eq 9 and the values of P and Q given in table 4.³

Although these values of P and Q are for potassium salts, consideration of the work of Harned and Hamer [11] and of Harned and Mannweiler [12] indicate that the difference between potassium and sodium salts is small, especially in dilute solutions.

The pH values for 0.01-*m* and 0.025-*m* borax buffers calculated by the two methods are given in table 5. In the case of 0.01-*m* borax buffer, the trend of the difference is about the same as that found for phthalate. For 0.025-*m* borax buffer, the agreement is considered satisfactory.

³ These values were obtained from Walter J. Hamer.

TABLE 4.—Values for P and Q for calculating pH by means of eq 9 ^a

Temperature C°	$\mu=0.005$		$\mu=0.01$		$\mu=0.02$		$\mu=0.05$		$\mu=0.10$	
	P	Q	P	Q	P	Q	P	Q	P	Q
0.....	0.0302	1.00046	0.0413	1.00065	0.0566	1.00087	0.0772	1.00107	0.0938	1.00123
5.....	.0303	1.00045	.0418	1.00064	.0567	1.00083	.0773	1.00102	.0942	1.00115
10.....	.0304	1.00044	.0418	1.00061	.0567	1.00079	.0776	1.00096	.0945	1.00108
15.....	.0307	1.00042	.0419	1.00059	.0568	1.00075	.0782	1.00094	.0955	1.00102
20.....	.0308	1.00041	.0422	1.00057	.0569	1.00072	.0789	1.00090	.0963	1.00096
25.....	.0313	1.00040	.0423	1.00055	.0575	1.00068	.0796	1.00085	.0976	1.00092
30.....	.0319	1.00039	.0431	1.00053	.0582	1.00065	.0807	1.00082	.0990	1.00088
35.....	.0322	1.00038	.0437	1.00051	.0587	1.00062	.0818	1.00079	1.002	1.00084
40.....	.0325	1.00036	.0441	1.00049	.0595	1.00059	.0829	1.00076	1.018	1.00080
45.....	.0327	1.00035	.0446	1.00047	.0601	1.00056	.0838	1.00073	1.029	1.00078
50.....	.0334	1.00033	.0451	1.00045	.0608	1.00053	.0849	1.00068	1.042	1.00074
55.....	.0339	1.00032	.0456	1.00042	.0613	1.00050	.0859	1.00066	1.054	1.00071
60.....	.0343	1.00031	.0459	1.00039	.0620	1.00047	.0869	1.00065	1.064	1.00069

^a Obtained from Walter J. Hamer; values at $\mu=0.05$ are listed by Hamer and Acree [9].

TABLE 5.—Comparison of the values for the pH of 0.01-*m* and 0.025-*m* solutions of borax free from chloride calculated by means of eq 7 and 9

Temperature °C	0.01- <i>m</i> borax buffer			0.025- <i>m</i> borax buffer		
	eq 7	eq 9	Difference	eq 7	eq 9	Difference
0	9.463	9.457	+0.006	9.460	9.457	+0.003
5	9.389	9.385	+ .004	9.394	9.392	+ .002
10	9.328	9.324	+ .004	9.331	9.330	+ .001
15	9.273	9.272	+ .001	9.274	9.273	+ .001
20	9.223	9.222	+ .001	9.221	9.221	± .000
25	9.177	9.176	+ .001	9.172	9.172	± .000
30	9.135	9.136	− .001	9.134	9.134	± .000
35	9.100	9.102	− .002	9.099	9.099	± .000
40	9.066	9.067	− .001	9.066	9.066	± .000
45	9.037	9.040	− .003	9.031	9.031	± .000
50	9.012	9.013	− .001	9.003	9.003	± .000
55	8.987	8.989	− .002	8.980	8.981	− .001
60	8.961	8.966	− .005	8.956	8.957	− .001

Plots of $\text{pH}_{(m_{\text{Borax}}=0.01, m_{\text{Cl}}=X)}$ and of $\text{pH}_{(m_{\text{Borax}}=0.025, m_{\text{Cl}}=X)}$ from 0° to 60° C as a function of the molality of sodium chloride are given in figures 2 and 3. The extrapolated values for the pH of 0.01-*m* solutions of borax free from added sodium chloride are plotted in figure 4. The relation between the pH of this solution and the absolute temperature T ($273.16 + \text{temperature in degrees centigrade}$) is expressed by the equation

$$\text{pH} = 2331.7/T + 0.017433T - 3.840, \quad (10)$$

with an average deviation of 0.001 unit from 0° to 60° C.

The values of C in eq 5 for 0.01-*m* and 0.025-*m* borax buffers are so nearly the same that it is possible to use the average value of C at each temperature in eq 7 to compute the pH of the solutions in series B ($m_{\text{Cl}}=0.01$). These values are shown graphically in figure 5. The pH

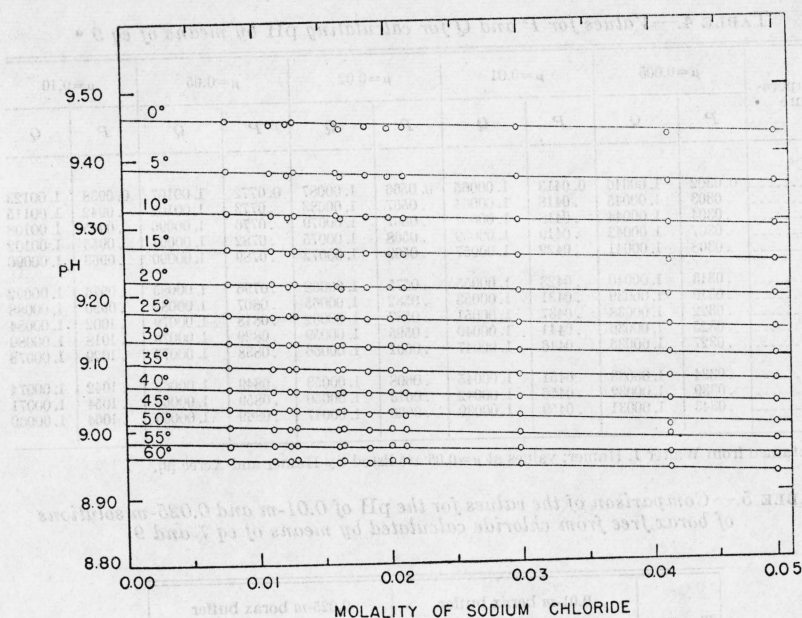


FIGURE 2.—Plot of the pH values from 0° to 60° C for 0.01-m solutions of borax, $\text{pH}(m_{\text{Borax}}=0.01, m_{\text{Cl}}=x)$ as a function of the molality of sodium chloride.

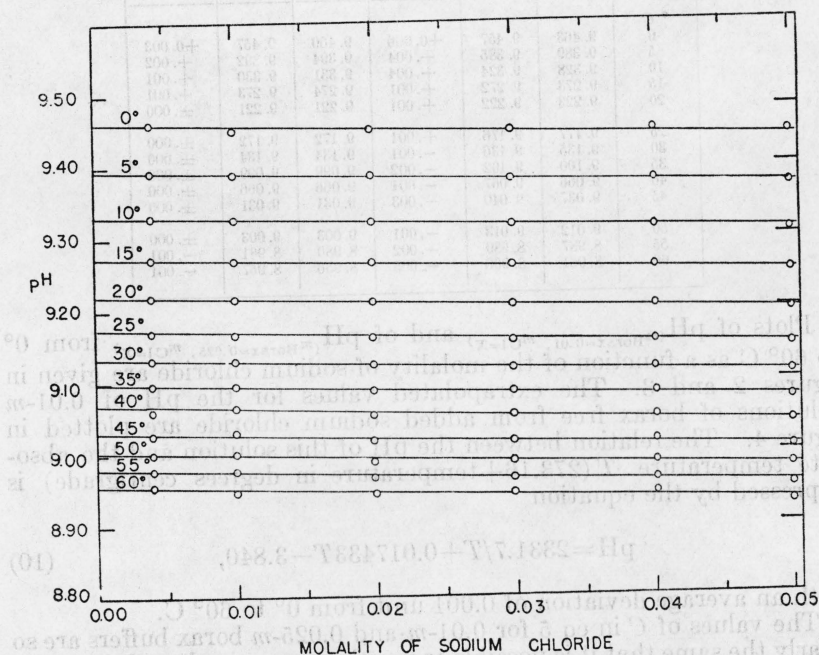


FIGURE 3.—Plot of the pH values from 0° to 60° C for 0.025-m solutions of borax, $\text{pH}(m_{\text{Borax}}=0.025, m_{\text{Cl}}=x)$ as a function of the molality of sodium chloride.

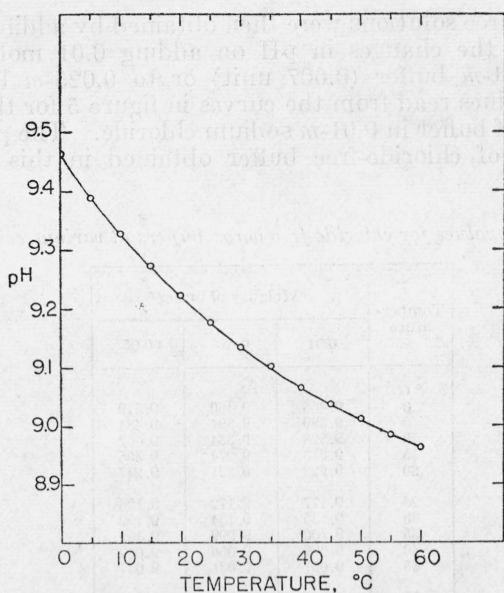


FIGURE 4.—pH of a 0.01-m solution of borax in the absence of sodium chloride, $\text{pH}_{(m_{\text{Borax}}=0.01, m_{\text{Cl}}=0)}$ of table 3, as a function of temperature.

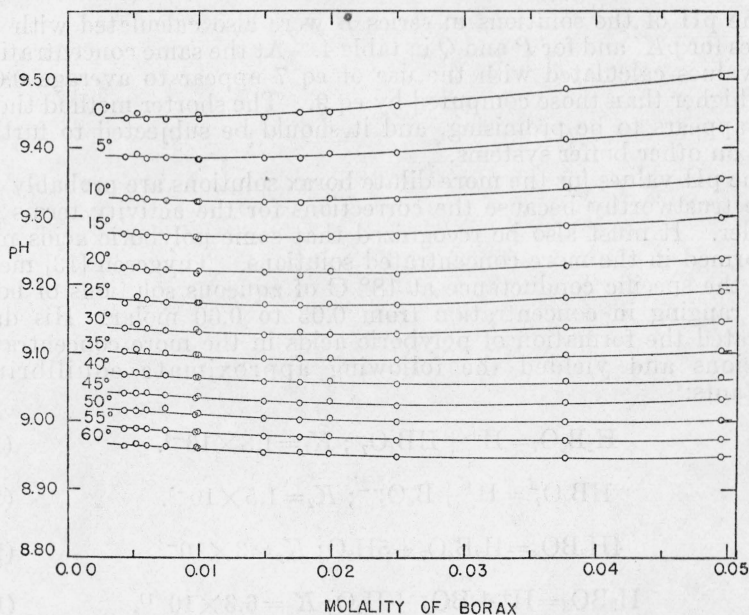


FIGURE 5.—Plot of the pH values from 0° to 60° C for various concentrations of borax buffer in 0.01-m sodium chloride solution.

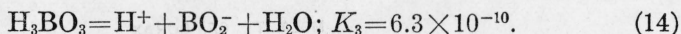
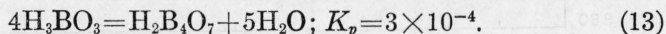
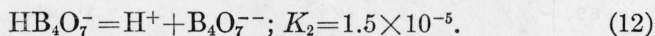
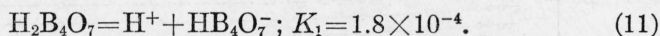
of the chloride-free solutions were then obtained by adding 0.006 unit, the average of the changes in pH on adding 0.01 mole of sodium chloride to 0.01-*m* buffer (0.007 unit) or to 0.025-*m* buffer (0.005 unit), to the values read from the curves in figure 5 for the particular concentration of buffer in 0.01-*m* sodium chloride. The pH of several concentrations of chloride-free buffer obtained in this manner are given in table 6.

TABLE 6.—pH values for chloride-free borax buffers at various concentrations

Temperature	Molality of buffer		
	0.01	0.025	0.05
° C			
0	9.463	9.460	9.512
5	9.389	9.394	9.434
10	9.328	9.334	9.362
15	9.273	9.274	9.305
20	9.223	9.221	9.247
25	9.177	9.172	9.196
30	9.135	9.134	9.152
35	9.100	9.099	9.109
40	9.066	9.066	9.069
45	9.037	9.031	9.037
50	9.012	9.003	9.008
55	8.987	8.980	8.980
60	8.961	8.956	8.956

The pH of the solutions in series *B* were also calculated with the values for pK' and for *P* and *Q* in table 4. At the same concentration, pH values calculated with the use of eq 7 appear to average 0.003 unit higher than those computed by eq 9. The shorter method therefore appears to be promising, and it should be subjected to further tests on other buffer systems.

The pH values for the more dilute borax solutions are probably the more trustworthy because the corrections for the activity terms are smaller. It must also be recognized that some polyboric acids may be formed in the more concentrated solutions. Thygesen [13] measured the specific conductance at 18° C of aqueous solutions of boric acid ranging in concentration from 0.03 to 0.60 molar. His data indicated the formation of polyboric acids in the more concentrated solutions and yielded the following approximate equilibrium constants:⁴



⁴ As an alternate explanation, Thygesen pointed out that the formation of a number of polymers such as $(\text{H}_3\text{BO}_3)_n$ could be postulated where $n=1, 2, 3, 4, 5$, etc. On this basis, it was concluded that the predominant polymer was the singly ionized form of triboric acid $\text{H}_3\text{B}_3\text{O}_7^-$ or B_3O_7^- . Unfortunately for both assumptions, at the higher concentrations of boric acid the increase in the apparent gross ionization constant of boric acid is paralleled by an increased uncertainty in the interpretation of the conductance data. The literature up to 1938 has been summarized by Thygesen.

The value for the first ionization constant, K_1 of eq 11, was estimated by analogy with the ratio of the two ionization constants of glutaric acid, a typical *organic* acid.

If the conclusions of Thygesen for free boric acid, pH approximately 4.5, are applied to solutions of boric acid and sodium borate of pH 9, the ionization constants given above suggest that in 0.01-*m* borax over 50 mole percent of the total boron is in the form of tetraborate ion, $B_4O_7^{--}$, and increases to 85 mole percent for a 0.05-*m* solution. The correctness of these estimated values is not supported by interpretations of the Raman spectra of solutions of borax [14].

From the work of Koltzoff [15] at 18° C, Latimer [16] estimated $K_1 \approx 10^{-4}$, $K_2 \approx 10^{-4}$, and, from the ratio $K_1/K_2 \approx 10^5$ for *inorganic* acids, $K_2 \approx 10^{-9}$ for the second ionization constant of tetraboric acid. Considering only the magnitude of these values, the concentrations of $H_2B_4O_7$, $HB_4O_7^-$, and $B_4O_7^{--}$ in a 0.01-*m* solution of borax are, respectively, 2×10^{-11} , and 3×10^{-6} , and 6×10^{-6} *m*. When the concentration of borax is 0.05 *m*, these values are increased to 1×10^{-10} , 2×10^{-4} , and 3×10^{-3} . These estimates are not in disagreement with the Raman data of Hibben [14], nor do they invalidate the essential conclusions of Thygesen that in 0.1-*m* boric acid, the above concentrations are very small (approximately 10^{-8} , 10^{-8} , and 10^{-12} *m*).

The neglect of the formation of these polymers affects only to a small degree the values for the pH of buffer-chloride solutions calculated by means of eq 7. For example, a solution containing 0.2 mole of boric acid and 0.1 mole of sodium hydroxide per liter of solution and in which the formation of polymers is ignored, $m_{H_3BO_3} = 0.1$, $m_{BO_2^-} = 0.1$, and the ionic strength is 0.1. If, on the other hand, the formation of polymers is recognized, $m_{B_4O_7^{--}} = 3 \times 10^{-3}$, $m_{HB_4O_7^-} = 2 \times 10^{-4}$, $m_{H_2B_4O_7} = 1 \times 10^{-10}$, $m_{H_3BO_3} = 0.10565$, and $m_{BO_2^-} = 0.08155$. (The concentrations of boric acid and of borate ion are not significant to the number of figures given but were calculated by difference.) The ionic strength in this case is 0.0938. The difference in the calculated pH of the two solutions is -0.003 unit when the same value for *C* in eq 7 is used in each case.

In view of the uncertainty in the exact value for the ionization and association constants in eq 11, 12, and 13, an error of ± 0.005 unit is assigned to the pH values of the 0.05-*m* solutions. It should be emphasized that the magnitude of the uncertainty from this cause drops rapidly with decreasing concentration and may be neglected for solutions as dilute as 0.02 *m*.⁵

IV. COMPARISON WITH THE pH VALUES IN THE LITERATURE

The pH values reported by a number of the earlier workers for the same concentration of buffer differ somewhat because of either the complete disregard of the potentials at the liquid junction or the use of the Bjerrum extrapolation [17] and the assumptions made in the "elimination" of these potentials. Further, it was not then recog-

⁵ The fact that it would be permissible to neglect the formation of polyboric acids in dilute solution was one of the factors in the decision to limit to 0.01 *m* the maximum concentration of borax for use as a pH standard. The pH values of the more concentrated solutions, however, are useful for comparison with other data in the literature.

nized that the potential of the calomel electrode was affected by lack of intimate contact between the finely divided mercury and the mercurous chloride [18], by exposure to air [19], the presence of small amounts of potassium bromide [20], and by thermal and electrical hysteresis [21]. The algebraic sum of these errors may have varied from one investigator to the next. A number of workers assumed that the pH at the midpoint of the neutralization of boric acid was equal to pK' and were not aware, for example, of the correction of approximately 0.1 pH unit in 0.05-*m* solutions of borax which would now be applied for the activity coefficient of the borate ion. For these reasons, it is difficult to apply suitable corrections to some of the earlier data. Some of the data, especially those obtained in the last few years, are recorded in sufficient detail to permit the recomputation

TABLE 7.—Comparison of the published pH values obtained for borax buffers by various workers

Year	Worker	Cell system	Temperature °C	m Borax	pH value		Remarks
					Previous worker	This paper	
1908.....	Schmidt and Finger [22].....	(a)	15.7	0.0625	9.27	9.34	Estimated value for col. 7.
1909.....	Sorensen [23].....	(b)	18	.05	9.24	9.215	
1915.....	Palitzsch [24].....		18	.05	9.24	9.270	
1916.....	Clark and Lubs [25].....	(c)	20	.0125	9.138	9.19	Estimated value for col. 7, 0.05- <i>m</i> KCl present.
1920.....	Walbum [26].....	(b)	{	10	.05	9.30	9.362
				20	.05	9.23	9.247
				30	.05	9.15	9.152
				40	.05	9.08	9.069
				50	.05	9.00	9.008
				60	.05	8.93	8.956
1922.....	Menzel [28].....	(a)	{	15	.005	9.23	9.280
				18	.005	9.20	9.249
1924.....	Prideaux and Ward [29].....		{	25	.005	9.15	9.184
				18	.005	9.02	9.248
1927.....	Kolthoff and Bosch [30].....	(d)	{	18	.01	9.19	9.243
				{	.02	9.20	9.242
					.005	8.95	8.966
					.01	8.89	8.961
1931.....	Fawcett and Acree [31].....	(a)	{	60	.02	8.88	8.957
				25	.0125	9.04	9.166
1931.....	Britton and Robinson [32].....	(e)	14	.0055	9.10	9.28	Estimated value for col. 7, authors used "universal buffer."
1934.....	Branch, Yabroff, and Bettman [33].....	(e)	25	.015	9.20	9.175	Value for <i>pK'</i> in col. 6 at midpoint of titration.
1937.....	Britton and Welford [34].....	(f)	{	12.5	.0333	9.27	9.314
				25	.0333	9.18	9.180
				34	.0333	9.10	9.100
				53	.0333	8.97	8.990
				{	.01	9.180	9.177
.02	9.168	9.173					
.03	9.170	9.176					
.04	9.175	9.185					
.65	9.180	9.195					
1937-38.....	Hitchcock and Taylor [35].....	(e)	{	.005	9.091	9.084	
				.01	9.078	9.081	
				.025	9.059	9.078	
				.0375	9.062	9.082	
				.05	9.070	9.085	
		(a)	{				

^a H₂/buffer|sat. KCl|0.1-*N* KCl|calomel.

^b H₂/buffer|1.75-*N* and 3.5-*N* KCl|0.1-*N* KCl|calomel.

^c H₂/buffer|sat. KCl|calomel.

^d H₂/buffer|sat. KCl|quinhydrone in 0.01-*N* HCl+0.09-*N* NaCl|Pt.

^e Sb, Sb₂O₃|"universal buffer"|sat. KCl|*N* KCl|calomel.

^f H₂/buffer|sat. KCl|*N* KCl|calomel.

^g H₂/buffer|sat. KCl|0.1-*N* HCl|H₂.

of pH values that take cognizance of present views concerning the interaction of ions in solutions.

In table 7 are given the values obtained by various workers for the pH of solutions of borax at various concentrations and temperatures, together with the available information concerning the type of cell used. The corresponding values obtained from the results of the present paper by the method of cells without liquid junction are given in column 7.

Recently, Hitchcock and Taylor [35] measured the electromotive force, E , at 25° and 38° C of hydrogen and calomel electrode cells containing various buffers at several dilutions. A combined function of the measured emf of the cell, the ionization constant of the buffer acid, the buffer ratio, and the first term, $A\mu^{1/2}$, of the Debye-Huckel expression was plotted against the ionic strength and extrapolated to $\mu=0$ to obtain the value of E_0 in the equation

$$\text{pH} = (E - E_0)/k, \quad (15)$$

where E_0 is the potential of the reference electrode including the liquid-junction potential. The pH values calculated for the borax buffers on the assumption that E_0 remains constant are given in column 6 of table 7.

The extrapolated value for E_0 obtained by this method appears to include the liquid-junction potential between an infinitely dilute buffer and saturated potassium chloride solution, and if the experimental measurements are extended to solutions that are sufficiently dilute, one should obtain values for E_0 that are independent of the buffer employed. In calculating the pH of buffers of finite concentration, however, the value for E_0 used as a constant in eq 15 should perhaps be replaced by $E_0' = E_{ref} + E_j$, where E_{ref} is the invariant potential of the reference electrode and E_j is the potential generated at the liquid junction between saturated potassium chloride and the particular concentration of buffer in question.⁶

From the pH-titration curve of boric acid with sodium hydroxide, Branch, Yabroff, and Bettman [33] reported 9.20 for the apparent ionization constant, $\text{p}K'$, at an ionic strength of 0.03. Two corrections to their data are permissible: (a) the accepted value at 25° C for the pH of the 0.05-*m* potassium acid phthalate is now 4.01 instead of 3.97 as employed by these authors, and (b) activity of the borate ion should be employed, rather than its gross concentration. The first of these corrections amounts to +0.04 pH unit and the second to -0.07 unit at a buffer concentration of 0.015 *m*. The corrected pH value is 9.17, which checks well with 9.175 interpolated from table 6.

The values given by Menzel [28] should be increased by 0.04 unit to compensate for the change from 3.97 to 4.01 for the pH of phthalate buffer. His value for the pH of a mixture of 0.01-*m* H_3BO_3 + 0.01-*m*

⁶ "The pH values given by Hitchcock and Taylor were calculated from their emf data without correction for liquid-junction potentials. For a given reference electrode at any one temperature, they employed only one E_0 value, which was the average of values given by the extrapolation of data obtained with several buffer systems", (personal communication from Dr. Hitchcock).

It should be emphasized that the numerical value calculated for the pH of a solution depends somewhat on the definition of the term "pH." The differences between columns 6 and 7 of table 7 should be construed in this light. For the justification of the basis used by this Laboratory in calculating the pH of solutions by the method of cells without liquid junctions, reference is made to the paper by Hamer and Acree [2]. It has been suggested that pH values defined on this basis be given a distinctive symbol such as pH to avoid confusion with the values of pH determined from cells with liquid junctions in which a uniform value is used for E_0 . (See footnote 2 of reference 2.)

NaBO_2 at 25°C then becomes 9.19, compared to 9.184 estimated from the method of cells without liquid junctions. The correction for the difference in the liquid junction potentials between phthalate and borate buffers at these concentrations is negligible [36].

Walbum [26] measured from 10° to 70°C the pH of mixtures of 0.1-*m* sodium borate and 0.1-*m* boric acid. These data are quoted extensively in Clark [27]. The correction for the liquid-junction potential was made by the extrapolation method of Bjerrum. The interpolated value at 25°C for the pH of 0.05-*m* borax is 9.19 from Walbum's data and 9.196 from table 6. Because additional details are lacking, it is difficult to make corrections at other temperatures.

Clark and Lubs [25] measured at 20°C the emf of a cell composed of a hydrogen electrode immersed in a buffer solution and a saturated calomel electrode and compared the potential of the latter with the tenth-normal calomel electrode. The emf data were then reported for the hydrogen and tenth-normal calomel electrode with a bridge of saturated potassium chloride. In addition to the customary correction to the observed emf,

$$E = \frac{2.3026RT}{2F} \log (760/(P-p)), \quad (16)$$

where P is the barometric reading and p is the vapor pressure of water in the solution, Clark and Lubs made a further correction for the concentration (the pressure) that the hydrogen gas would have if it were at 0°C instead of the temperature of the measurements. On the basis of the single correction (eq 16) one obtains 0.56890 v and 0.86907 v, respectively, at 20°C for the measured emf for 0.05-*m* potassium acid phthalate and for 0.025-*m* $\text{H}_3\text{BO}_3 + 0.025\text{-}m$ $\text{NaBO}_2 + 0.05\text{-}m$ KCl. The present value for the pH of the 0.05-*m* phthalate buffer at 20°C is 4.001 [10], determined by the method of cells without liquid junction. The combination of 0.56890 v for the emf and of 4.001 for the pH yields 0.33626 v for $E_{\text{ref}} + E_j$ of 0.05-*m* phthalate buffer in contact with saturated potassium chloride. The pH value for 0.025-*m* $\text{H}_3\text{BO}_3 + 0.025\text{-}m$ $\text{NaBO}_2 + 0.05\text{-}m$ KCl is therefore 9.163. The value estimated from tables 3 and 6 for this buffer is 9.19.

Sørensen's measurements at 18°C [23] made use of the tenth-normal calomel electrode and the Bjerrum extrapolation. The potential of the reference electrode ($E_{\text{ref}} + E_j$) was determined by replacing the buffer solution with 0.01-*m* HCl + 0.09-*m* NaCl. The value 9.24 at 18°C was obtained for the pH of 0.05-*m* borax. One correction to the above work involves a change in pH value of the hydrochloric acid-sodium chloride mixture. Sørensen used 2.038; the current treatment of electrolytes yields 2.014 [37], from which $E_{\text{ref}} + E_j = 0.3389$ v. A second correction involves the difference in the values for $(E_{\text{II}} - E_{\text{I,II}})/k$ between the hydrochloric acid-sodium chloride solution and the borax buffer each in contact with a saturated solution of potassium chloride. This correction is estimated to be -0.02 pH unit [36]. The corrected value for the pH of Sørensen's borate buffer is therefore 9.20 with a possible uncertainty of ± 0.02 unit. From table 6 the pH for a solution of borax of the same concentration is 9.215.

It is therefore evident that to a large extent the discrepancy between the pH values of comparable buffers determined by the method of cells (a) with liquid junction and (b) without liquid junction is due for the most part to the manner employed in the first method for making the correction for the liquid-junction potential. Considering the variety of methods by which the corrections were made, the agreement is satisfactory.

V. RECOMMENDED BUFFER SOLUTION

While any of the concentrations of buffer listed in table 6 can be used for the preparation of solutions of a definite pH value, it is believed that, because of the closer approach to an ideal behavior of the ions in a dilute solution, the most practical concentration is a mixture of 0.02 mole of boric acid and 0.02 mole of sodium borate dissolved in 1 kg of water. This solution can be prepared by dissolving 3.81 g of borax (0.01 mole) in freshly boiled distilled water in a 1-liter volumetric flask and filling the latter to the mark.⁷ The resistance of solutions of borax to change in pH on dilution is large and permits the use of concentration on the volume rather than on weight basis, the difference in this case being less than 0.001 pH unit. The high molecular weight of borax, 381.434, is another advantage. The pH values from 0° to 60° C for this solution are the same as those given in column 2 of table 6.

The 0.01-*m* borax buffer forms a useful standard for the calibration of pH meters that use the Corning type 015 glass electrode because the "sodium error" for this buffer is only 0.01 pH unit. It is recommended that all types of pH meters be calibrated with at least two buffers spaced as widely apart as possible on the pH scale. In addition to 0.05-*m* potassium acid phthalate, pH=4.005 at 25° C, for which the correction $(E_{\text{I}} - E_{\text{II}})/k$ is negligible, a number of other standard buffers have been recommended [36].

The authors are indebted to Cyrus G. Malmberg for the preparation and measurement of the conductance of the distilled water used in these experiments.

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⁷ The borax (sodium tetraborate decahydrate) should be recrystallized from water and washed with alcohol and ether as described in a previous publication [1]. The pH of the distilled water should be between 6.5 and 7.5 if a reproducibility of ± 0.002 in the pH of the buffer solution is desired. For ordinary purposes, ± 0.05 unit, air-equilibrated water of pH 5.5 (which may contain a trace of ammonia as well as carbon dioxide) may be used, and the salt need be weighed only to ± 0.1 g.

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